by repeated small additions of water to give needles, mp 69–70 °C. Difficulties encountered were typical of the unsymmetrical low melting salts of **2**.

Borane cations were prepared by adding dropwise $^1/_2$ molar equiv of iodine in chloroform solution to a chloroform solution of **3**. An equimolar amount of ligand (trimethylamine, **2**, or **3**) was added, and the mixture was allowed to stand for 12 h. Solvent was removed under vacuum and the residual oil taken up in water and metathesized with an aqueous solution of ammonium hexafluorophosphate. The $PF_6^-$ salts precipitated as oils that were crystallized by cooling and scratching the vessel walls with stirring rod. Recrystallization from

water/ethanol (ca. 3:1) gave soft crystals.

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(5) Miller, N. E. *Inorg. Chem.* **1977**, *16*, 2664.

# Correspondence

## Comparisons of Experimental Activation Parameters for the Co(terpy)₂²⁺–Co(bpy)₃³⁺ Redox Reaction with the Marcus Theory and the Fe(phen)₃²⁺,³⁺ System

*Sir:*

The Marcus theory[1] is most useful for examining the activation free energy and its components for adiabatic outer-sphere redox reactions through

$$k_{12} = Z \exp(-\Delta G^*_{12}/RT) \quad (1)$$

where

$$\Delta G^*_{12} = \omega_{12} + \lambda_{12}/4 + \Delta G°_{12}/2 + (\Delta G°_{12})^2/4\lambda_{12}$$

with $k_{12}$, the cross-reaction rate constant, $Z$, the collision frequency in solution ($10^{11}$ $M^{-1}$ $s^{-1}$), and $\omega_{12}$, the work term, and all others have their usual meaning. Due to the reasonably good agreement between the measured redox rate constant and the rate constant calculated from the Marcus theory for the Co(terpy)₂²⁺–Co(bpy)₃³⁺ system in water,[2] the comparison is extended here to include activation parameters. The Marcus theory predicts a simple relationship between the activation free energy of a cross reaction ($\Delta G^*_{12}$) and the activation free energies of the self-exchange redox reactions of the reactants ($\Delta G^*_{11}$, $\Delta G^*_{22}$):

$$\Delta G^*_{12} = (\Delta G^*_{11} + \Delta G^*_{22})/2 + \Delta G°_{12}(1 + \alpha)/2 \quad (2)$$

and

$$\alpha = \Delta G°_{12}/4(\Delta G^*_{11} + \Delta G^*_{22})$$

Marcus and Sutin[3] showed that the activation parameters $\Delta H^*_{12}$ and $\Delta S^*_{12}$ for an electron-transfer reaction can be obtained by differentiating eq 2 with respect to temperature which yields

$$\Delta H^*_{12} = [(\Delta H^*_{11} + \Delta H^*_{22})/2](1 - 4\alpha^2) + (\Delta H°_{12}/2)(1 + 2\alpha) \quad (3)$$

and

$$\Delta S^*_{12} = [(\Delta S^*_{11} + \Delta S^*_{22})/2](1 - 4\alpha^2) + (\Delta S°_{12}/2)(1 + 2\alpha) \quad (4)$$

and that the relationships between the Marcus parameters and

the corresponding experimental terms are

$$\Delta G^* = \Delta G^\ddagger + RT \ln (hZ/\kappa T)$$
$$\Delta H^* = \Delta H^\ddagger + RT/2 \quad (5)$$
$$\Delta S^* = \Delta S^\ddagger - R \ln (hZ/\kappa T) + R/2$$

An activation free energy ($\Delta G^\ddagger$) of 14.2 kcal/mol is obtained from eq 2 and 5 which is in good agreement with the experimental value of 13.6 kcal/mol.[2] The activation enthalpy and entropy of the cross reaction could not be compared due to the lack of data on the Co(terpy)₂²⁺,³⁺ self-exchange. Consequently, eq 3 and 4 were used to estimate these parameters for this self-exchange redox system. With the activation parameters from the Co(terpy)₂²⁺–Co(bpy)₃³⁺ system[2] and the Co(bpy)₃²⁺,³⁺ self-exchange,[4] $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the Co(terpy)₂²⁺,³⁺ self-exchange are 9.4 kcal/mol and −12 eu, respectively. These values appear to be good estimates since their use in the Co(terpy)₂²⁺–Co(phen)₃³⁺ system[2] gave excellent agreement between the observed and calculated activation parameters obtained from eq 3 and 4.

The components of the activation free energy can be estimated from eq 1 which shows that the reorganization parameter $\lambda_{12}$ can be determined if $\omega_{12}$ and $\Delta G°_{12}$ are known or can be calculated. The experimental value for $\Delta G°_{12}$ is −0.69 kcal/mol[2] and the work term was estimated under the same experimental conditions from the expression[5]

$$\omega_{12} = (Z_1Z_2/D\bar{r}) \exp[-(8\pi e^2N^2\mu/10^3DRT)^{1/2}D\bar{r}] \quad (6)$$

with all terms having their usual meaning. Eq 6 yields a value of 0.62 kcal/mol for $\omega_{12}$ from which $\lambda_{12}/4$ is calculated to be 11.2 kcal/mol with use of eq 1. This result is in good agreement with the mean value of the reorganization parameters of the self-exchange redox reactions of the reactants which is 11.7 kcal/mol obtained from

$$\lambda_{12} = (\lambda_{11} + \lambda_{22})/2 \quad (7)$$

Both $\lambda_{11}$ and $\lambda_{22}$ were estimated from their respective $\Delta G^*$ values where $\Delta G°$ is zero and the work terms were assumed to be similar to that of the cross reaction. Finally, Marcus considers the reorganization parameter to be composed of an inner-sphere ($\lambda_i$) and outer-sphere $\lambda_o$ component where

$$\lambda = \lambda_i + \lambda_o \quad (8)$$

and

(1) Pelizzetti, E. *Inorg. Chem.* **1979**, *18*, 1386 and references therein.
(2) Farina, R. D.; Wilkins, R. G. *Inorg. Chem.* **1968**, *7*, 514.
(3) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213.

(4) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.
(5) Reynolds, W. L.; Lumry, R. W. "Mechanisms of Electron Transfer"; Ronald Press Co.: New York, 1966; p 123.

Table I. Comparison of Observed and Calculated Rate Parameters for the Co(terpy)$_2$$^{2+}$-Co(bpy)$_3$$^{3+}$ and Fe(phen)$_3$$^{2+}$-Fe(phen)$_3$$^{3+}$ Systems in Water

| parameter | Co(terpy)$_2$$^{2+}$-Co(bpy)$_3$$^{3+}$ | Fe(phen)$_3$$^{2+}$-Fe(phen)$_3$$^{3+}$ |
|---|---|---|
| $\bar{r}$, Å | 14 | 14 |
| $\Delta G^*_i$, kcal/mol | 7.9 | 3.2 |
| $\Delta G^*_o$, kcal/mol | 3.3 | 3.3 |
| $k_{calcd}$, M$^{-1}$ s$^{-1}$ | 32 | 6 × 10$^7$ |
| $k_{obsd}$, M$^{-1}$ s$^{-1}$ | 64$^a$ | 3.3 × 10$^8$ $^b$ |

$^a$ Reported at 0 °C in ref 2.    $^b$ Reported at 25 °C in ref 7.

$$\lambda_o = (\Delta Z)^2 e^2 (1/2r_1 + 1/2r_2 - 1/\bar{r})(1/D_{op} - 1/D) \qquad (9)$$

so that each component can be estimated. All terms in eq 9 have their usual meaning. A direct estimate of $\lambda_i$ requires knowledge of force constants and bond lengths of these cobalt reactants in water which are unavailable. However, using reactant radii of 7 Å[6] with an $\bar{r}$ value of 14 Å allows $\lambda_o$ to be estimated from which $\lambda_i$ can be obtained by using eq 8. The values for the inner-sphere ($\lambda_i/4$) and outer-sphere ($\lambda_o/4$) reorganization energies are 7.9 and 3.3 kcal/mol, respectively. A comparison of these results with the Fe(phen)$_3$$^{2+,3+}$ system is made in Table I where a $k_{obsd}$ of 3.3 × 10$^8$ M$^{-1}$ s$^{-1}$ has been reported for the redox rate constant.[7] The comparison shows that although the outer-sphere reorganization energies are similar, large differences exist in the inner-sphere reorganization energy where the cobalt system is larger by about 4.7 kcal/mol. A large inner-sphere reorganization energy has been proposed by Sutin[8] for these type systems of cobalt since the electron being transferred is removed from an e$_g$ orbital of the reductant where the increased electron density on the metal

ion cannot be removed via a M→L $\pi$-bonding path as in Fe(phen)$_3$$^{2+}$. Moreover, e$_g$ electrons are more intimately involved in $\sigma$ bonding between the central metal ion and the coordinated ligands so that larger changes in the metal–ligand bonding are expected compared to the transfer of an t$_{2g}$ electron. The large difference in the inner-sphere reorganization energies may simply reflect this and could be responsible for the relatively slow redox rate observed in these cobalt systems. Unlike the Co(NH$_3$)$_6$$^{2+,3+}$ self-exchange where the slowness has been attributed to energy differences between the spin states of the reactants,[9] both cobalt complexes are low spin.[10] The possibility of some nonadiabaticity brought about by weak interactions between reactants cannot be ruled out as one factor which could contribute to the slowness of the redox rate. Under these conditions, the outer-sphere rate constant would be given by $k = pZ \exp(-\Delta G^*/RT)$ with $p$ being the probability of electron transfer in the activated complex. However, similar arguments would be applicable to the self-exchange reactions of the reactants, and if all reactions are uniformly nonadiabatic, i.e., $p_{12}^2 = p_{11}p_{22}$, the Marcus rate equations would still predict well as observed.

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(7) Ruff, I.; Zimonyi, M. *Electrochim. Acta* **1973**, *18* (7), 515.
(8) Sutin, N. *Inorg. Biochem.* **1973**, *2*, 631.
(9) Stynes, H. E.; Ibers, G. A. *Inorg. Chem.* **1971**, *10*, 2304.
(10) Davies, G.; Warnqvist, B. *Coord. Chem. Rev.* **1970**, *5*, 349.

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# Additions and Corrections

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**Eric A. Maatta, Barry L. Haymore,\* and R. A. D. Wentworth\*:** Syntheses of Mo(NC$_6$H$_5$)X$_2$(S$_2$CN(C$_2$H$_5$)$_2$)$_2$ (X = Cl, Br) and the Structure of Mo(NC$_6$H$_5$)Cl$_2$(S$_2$CN(C$_2$H$_5$)$_2$)$_2$·CHCl$_3$.

Page 1057. In Table II, the $x$ coordinate for atom C(10) should 0.4884 (6).

Page 1058. In Table V, Mo–Cl(1) should be 2.469 (1) Å and Mo–Cl(2) should be 2.467 (1) Å.—Barry L. Haymore